Effect of Surface Freezing on Stability of Oil-in-Water Emulsions

*Yuhei Tokiwa, Hiromu Sakamoto, Takanori Takiue, Makoto Aratono, Hiroki Matsubara**

Department of Chemistry, Faculty of Science, Kyushu University, 744 Motooka Nishi-ku Fukuoka 819-0395, Japan

Colin D. Bain

Department of Chemistry, Durham University, Stockton Road, Durham, DH1 3LE, U. K.

Corresponding Author

*h.matsubarascc@chem.kyushu-univ.jp

ABSTRACT

Penetration of alkane molecules into the adsorbed film of a cationic surfactant gives rise to a surface freezing transition at the alkane–water interface upon cooling. In this paper, we show that surface freezing of hexadecyltrimethylammonium chloride (CTAC) at the tetradecane-water interface stabilizes oil-in-water (OW) emulsions. For concentrations of CTAC near the critical micelle concentration, an OW emulsion coalesced readily above the surface freezing transition whereas the OW emulsion was stable in the surface frozen state. There was a discontinuous change in the stability of the OW emulsion at a temperature very close to the surface phase transition temperature as determined by interfacial tensiometry and ellipsometry on a planar oil-water interface. The mechanical elasticity of the surface frozen layer opposes film drainage and density fluctuations that could lead to rupture, and is the most likely cause of the enhanced emulsion stability.

INTRODUCTION

Adsorbed films of soluble amphiphiles exist in three different physical states called gaseous, expanded, and condensed states, which respectively correspond to two-dimensional gas, liquid, and solid phases.[1-9] Among these, the condensed film formation has largely been limited to sparingly water-soluble nonionic amphiphiles such as long-chain alkanols.[1,2,4-9] In 2000, McKenna et al. reported that a mixed monolayer of hexadecylltrimethyl ammonium bromide (CTAB) and *n*-tetradecane (C14) underwent a first-order freezing transition at the air–water interface upon cooling.[10] Subsequently, Sloutskin et al. carried out surface tension and X-ray reflectivity measurements on mixed monolayers of CTAB and the series of *n*-alkanes and confirmed that the thickness of the surface frozen monolayers increased with *n*-alkane chain length for dodecane – heptadecane and found that the low-temperature phase was a hexagonally packed two-dimensional solid phase a single monolayer thick, with upright, conformationally ordered chains.[11,12] The structures of the surface frozen layer is similar to those observed for surface frozen monolayers at the air–alkane[13] and air–alcohol[14] interfaces. For pure linear alkanes, the surface freezing transition occurs between 16 and 50 carbons in length and the surface transition temperatures are up to 3 °C above the bulk melting point. The presence of surfactant induces a surface freezing transition for shorter alkanes (C14) and at even higher temperatures by augmenting the lateral van der Waals interactions between the hydrocarbon chains of surfactant and alkane. Moreover, the surface tension can be varied widely with surfactants.

Lei and Bain showed that a surface frozen phase also exists at the liquid tetradecane–water interface in the presence of CTAB, despite the absence of surface freezing at a pure alkane-water

interface.[15] A surprising feature of the surface freezing transition is that the interfacial density of surfactant almost remains constant at the surface freezing transition: the increase in hydrocarbon chain density required for the formation of a solid monolayer is attained by the penetration of alkane molecules into the adsorbed film. The generality of the surface freezing transition was later confirmed for CTAB and octadecyltrimethylammonium bromide (STAB) with alkanes of various chain lengths by Deutsch and co-workers using interfacial tensiometry and X-ray reflectivity.[16,17]

These findings motivated us to investigate the effect of the surface freezing transition on the stability of OW emulsions. The high Krafft temperature of CTAB (25 ^{o}C) is a limitation in studies of emulsion stability, but the chloride ion counterpart, CTAC has a much lower Krafft temperature (2 ^{o}C) and therefore allows the study of emulsion stability over a much larger temperature range.[18,19] We have shown previously that CTAC and CTAB exhibit surface freezing transitions within 1–2 ^{o}C for a range of alkanes.[20] We also examined the preferential adsorption of alkanes at the oil−water interface for the binary mixtures of *n*-dodecane (C12), C14, and *n*-hexadecane (C16) in the presence of CTAB and found that the surface frozen film was mainly composed of CTAB and longer chain alkanes while the shorter alkanes were expelled from the interface to the bulk oil phase.[20] C16 has its melting point at 17−18 ^{o}C and the surface freezing transition of the CTAB adsorbed film is interrupted by the freezing of the bulk alkane. However, the preferential incorporation of C16 in the adsorbed film raises the surface freezing transition temperature in the alkane mixtures and therefore is also useful to expand the temperature range of the surface frozen film. In this paper, we first show that the kinetic stability of an oil-in-water emulsion is remarkably enhanced when a surface frozen film of CTAC is formed at the C14–water interface and then confirm this result by observing C14-C16 mixtures

with a varying mixing ratio. Finally, the high mechanical elasticity of the surface frozen layer and resultant slow film drainage is proposed as the primary cause of the enhanced emulsion stability after various mechanisms of emulsion stabilization were considered.

EXPERIMENTAL SECTION

Materials: CTAC (Nacalai tesque Co. Ltd., >99%) was purified eight times by recrystallization from a mixture of acetone and ethanol. Oil-soluble impurities were removed by the extraction 6 times from hexane. No minimum was observed in the surface tension vs. concentration curve around the critical micelle concentration (cmc). All samples were prepared with Milli-Q water. *n*-Tetradecane (Nacalai tesque Co. Ltd., >99%) was purified by the fractional distillation under reduced pressure. Their purities were confirmed by measurement of the oil–water interfacial tension and estimated to be >99.9% by GC.

Interfacial tensiometry: Interfacial tension, γ, was determined by the analysis of the shape of a pendant drop of surfactant solution hanging on a glass capillary in the oil phase by varying temperature, T, at constant CTAC molality in aqueous solution, m. The experimental error of the interfacial tension was within 0.1 mN m^{-1}.

Ellipsometry: Ellipsometry was performed by a Picometer Ellipsometer (Beaglehole Instruments Wellington, NZ) equipped with a HeNe laser at 632.8 nm. The surfactant solution of about 20 mL was contained in a 6.5 cm diameter glass dish and the same amount of oil was poured onto it. The dish was placed in a brazen jacket then thermostatted by circulating temperature-controlled water. The coefficient of ellipticity, $\bar{\rho}$, defined as the imaginary part of r_p/r_s at the Brewster

angle was recorded (r_p and r_s are the complex Fresnel reflection coefficients for p- and s-polarized light). The laser beam was applied to the air-alkane interface at ~75° and the refracted light hit the alkane–water interface at incident angle of ~43°, which is the Brewster angle of alkane–water interface. The precision of $\bar{\rho}$ was typically $\pm 1 \times 10^{-5}$, except in the vicinity of the phase boundaries where larger fluctuations were observed.

RESULTS AND DISCUSSION

Figure 1(A) shows the interfacial tension (γ) vs. temperature (T) curve for the CTAC adsorbed film at a planar C14–water interface. The concentration of CTAC in the aqueous phase was set to m = 1.2 mmol kg^{-1} which was close to but slightly smaller than the critical micelle concentration (1.3 mmol kg^{-1}).[18] The surface tension has a clear kink at 9.3 ^{o}C corresponding to the phase transition between surface liquid and surface frozen states. A discontinuous change in the coefficient of ellipticity at the same temperature as the kink in the γ vs. T curve supports the existence of the surface phase transition. Figure 1(B) displays the interfacial tension as a function of temperature for varying CTAC concentrations, showing that the surface phase transition temperature decreases with decreasing concentration, in agreement with previous studies.[15] For details of the interpretation of interfacial tension and ellipsometry data, see refs. (15) and (20).

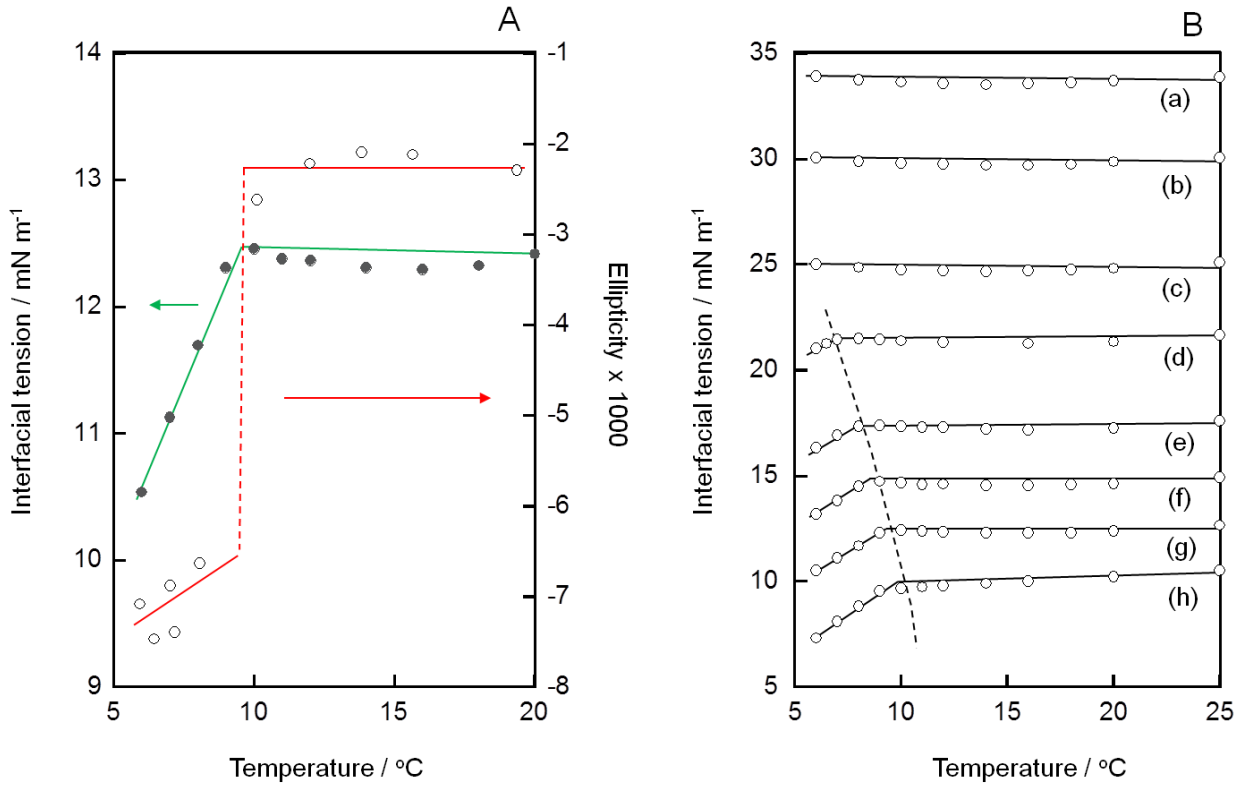

Figure 1. (A) Interfacial tension vs. temperature curve (green) and ellipticity vs. temperature curve (red) for the CTAC adsorbed film at the tetradecane-water interface. Initial CTAC concentration in aqueous phase = 1.2 mmol kg^{-1}. (B) Effect of CTAC concentration on the interfacial tension of the tetradecane–water interface as a function of temperature: (a) 0.10, (b) 0.20, (c) 0.40, (d) 0.55, (e) 0.80, (f) 1.00, (g) 1.20, (h) 1.50 mmol kg^{-1}. The dashed line indicates the surface phase boundary.

Figure 2 shows the height of the emulsion phase plotted as a function of time, together with pictures of OW emulsion samples that had been thermostatted 24 hours at 7.0 and 15.0 ^{o}C after preparation. We stirred equal volumes (5 ml) of C14 and 1.3 mmol kg^{-1} CTAC aqueous solution

for 1 min by a vortex mixer in a test tube. For the sample kept at 7.0 ^{o}C, which is in the temperature range of the interfacial frozen state, the volume of the OW emulsion (the turbid part of the sample) remained almost constant for 24 hours. For the emulsion at 15.0 ^{o}C, in which the interface is in its liquid state, bulk oil phase started to appear above the OW emulsion immediately and the volume of the emulsion decreased continuously with time. The phase tubes shown in Figure 3 for emulsions aged at different temperatures show that the stability of the emulsion changes discontinuously between 9 and 10 ^{o}C corresponding to the surface phase transition temperature identified by tensiometry and ellipsometry at a planar oil–water interface. Differential scanning calorimetry of an emulsion sample confirmed the existence of the surface freezing transition in the emulsion from an exothermic peak at about 9 ^{o}C in the heating cycle, which is different from the melting points of both bulk C14 (5 ^{o}C) and the solid hydrates of CTAC (2 ^{o}C). We note that adsorption of the surfactant at the oil–water interface in emulsions may significantly deplete the aqueous phase of CTAC, so the phase transition temperatures measured in different experiments will not be identical.

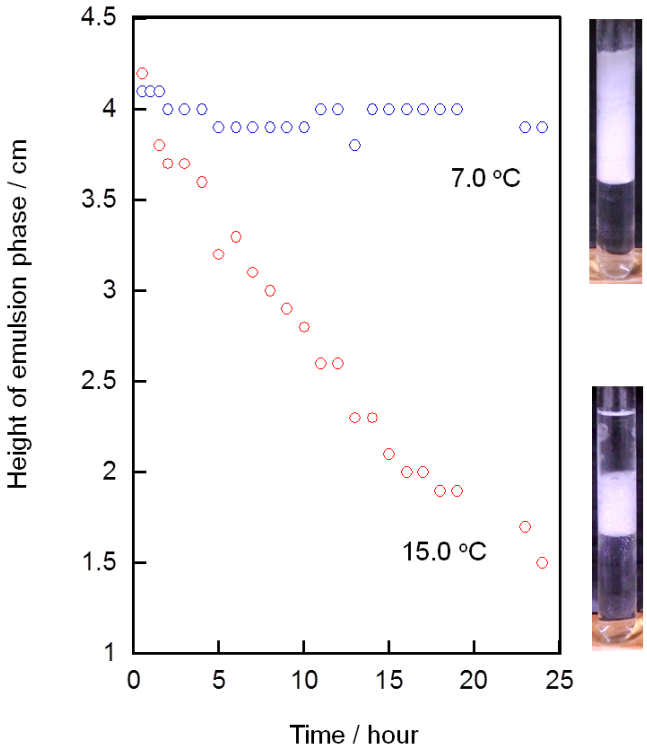

Figure 2. Height of emulsion phase plotted as a function of time and pictures of OW emulsion samples thermostatted for 24 hours at 7.0 and 15.0 ^{o}C after preparation.

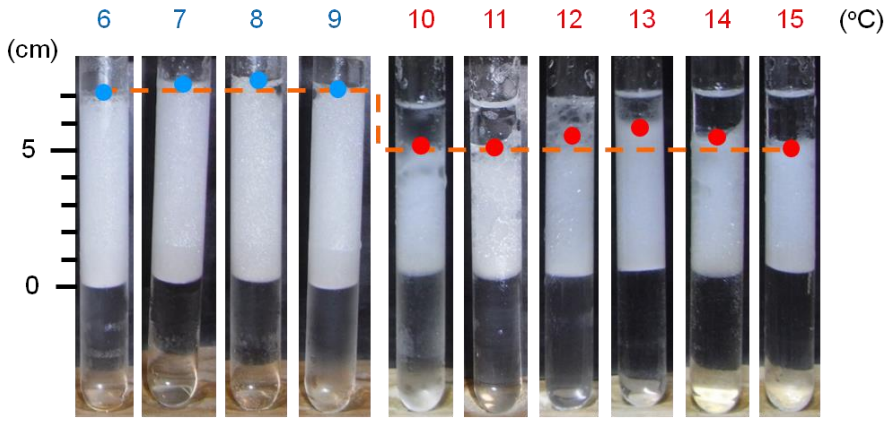

Figure 3. Pictures of OW emulsion samples made by stirring equal volumes of tetradecane and 1.3 mmol kg^{-1} CTAC aqueous solution. Samples were thermostatted for 24 hours at temperatures given in the figure. Blue and red dots are guide for the eye.

Similar results were observed for the emulsion stability of alkane mixtures. Figure 4(a)–(c) shows the pictures of emulsion samples prepared with C14-C16 mixtures at molar ratios of 8:2, 6:4, and 4:6, respectively. The surface freezing temperature separately measured by interfacial tensiometry and ellipsometry, denoted by red triangles in Figure 4, rose with increasing C16 composition in the bulk oil. The temperatures where the stability of the emulsion changed coincided with the surface freezing temperatures.

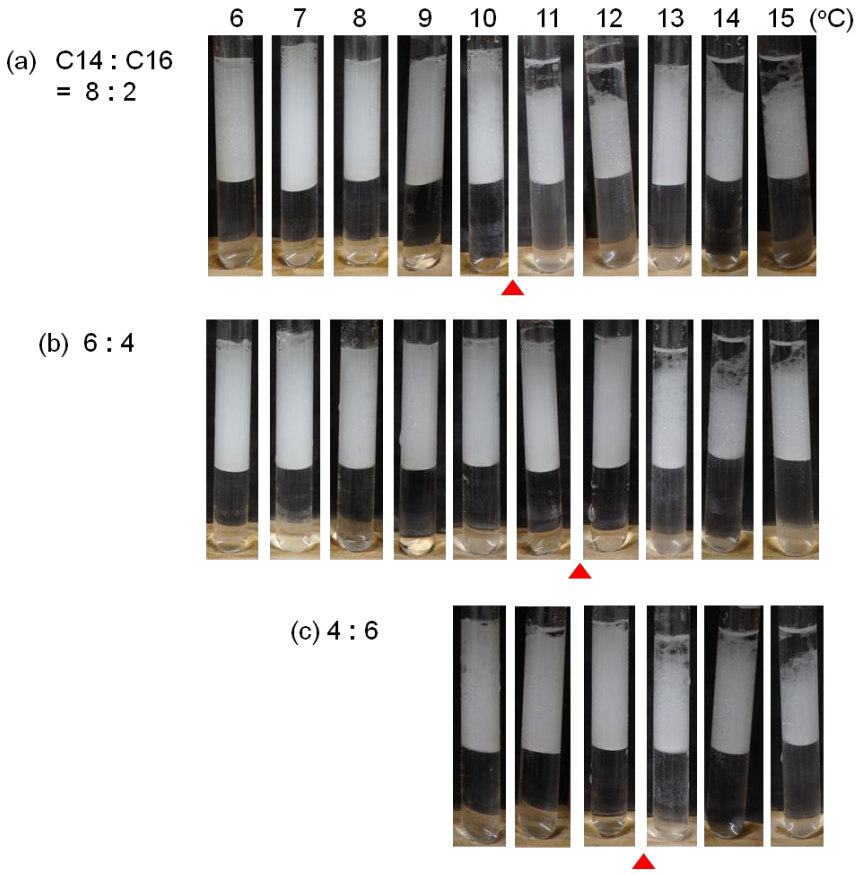

Figure 4. Pictures of OW emulsion prepared with the given mixing ratio of tetradecane (C14) and hexadecane (C16). The initial concentration of CTAC is 1.3 mmol kg^{-1} for all samples. Samples were thermostatted for 24 hours at temperatures given in the figure.

The enhanced stability of the emulsion in the surface frozen phase is most marked at concentrations around the cmc (see Supplementary Information). At higher concentrations, the interface is saturated with CTAC and both emulsions in the liquid and surface frozen states are stable for 24 hours. At much lower concentrations, the surface frozen phase ceases to be thermodynamically stable (Figure 1B) and the emulsion is observed to collapse.

We consider three different destabilization mechanism of general OW emulsions to ascertain whether they can explain the observed stability of OW emulsions with frozen surface layers. The first is Ostwald ripening by which large droplets grow at the expense of smaller ones. This process is formalized as the Kelvin equation,[21,22]

$$c(r) = c_\infty \exp\left(\frac{2\gamma V_m}{rRT}\right) \cdots\cdots (1)$$

where $c(r)$ is the solubility of oil droplet of radius r, c_∞ is the solubility of a macroscopic droplet, and V_m is the molar volume of the oil. Applying the interfacial tension γ at the surface freezing transition temperature shown in Figure 1 and other required parameters,[23] we find that the solubility difference is negligible (<0.1%) for the droplet sizes of 10–100 μm in our experiments (see Supporting Information). Furthermore, the interfacial tension is continuous at the phase transition temperature while the emulsion stability changes discontinuously. Therefore, in the present study, Ostwald ripening is not a factor in the enhanced stability of OW emulsions with frozen surface layers.

The second factor to be considered is DLVO interactions between emulsion droplets.[24] In general, the surface density of surfactants increases at surface freezing transitions.[20] Hence, if

the interfacial density of CTAC were to increase at the surface phase transition, it might lead to increased stability within DLVO theory through an increase in surface charge density. However, as shown in Figure S1 (A) in Supplementary Information, the difference in the surface density between 7.0 and 15.0 ^{o}C is no more than 0.3 μmol m^{-2}. Converting this surface excess into the surface charge density, this change is roughly equal to 0.03 C m^{-2}, which hardly varies the electrical double layer potential. Furthermore, previous studies on monolayers at the air–water interface have shown a higher degree of counterion binding to the solid than to the liquid phase.[25] The same behavior at OW interfaces would decrease rather than increase emulsion stability. It is therefore unlikely that double-layer repulsions are responsible for the enhanced emulsion stability displayed in Figures 2 and 3.

Finally, we considered how the rheological response of the interface may hinder droplet coalescence. The rheological property of interfaces that is most often associated with the stability of foams and emulsions is the dilational (visco) elasticity, which can be obtained from measurements of the interfacial tension response to surface area perturbations. Bergeron has argued that dilational elasticity suppresses fluctuations that lead to film rupture.[26] It is also well-known that the drainage from foam lamellae into the Plateau border, which controls the pathway to film thinning and rupture, is strongly influenced by the film rigidity. Films with effectively rigid surfaces exhibit comparatively slow drainage compared with mobile interfaces, by an order of magnitude or more in rate.[27,28] However, in a study of the liquid–solid surface phase transition of a1-dodecanol film at the air-water interface, Muñoz et al [29] found that the dilational elasticity did not change at the surface freezing transition in the range of frequencies studied by surface quasi-elastic light scattering (SQELS, 5–60 kHz) and electrocapillary wave (ECW, 0.02–2 kHz) methods. They proposed the exchange of alcohol molecules between the

monolayer and the sub-phase to explain the invariance of the elasticity at the surface phase transition. Casson et al. demonstrated by sum-frequency spectroscopy that the phase transition in dodecanol monolayers is associated with surprisingly little change in the molecular-level order of the monolayer.[31] Conversely, for CTAB/tetradecane monolayers on water, surface freezing causes a large change in chain ordering,[10] indicating that linear alcohols are not a perfect analogue of mixed surfactant/alkane phases from the view point of molecular ordering and resultant mechanical properties of the interfacial films. Capillary wave scattering experiments on mixed surfactant/alkane monolayers are currently under way in our laboratory.

A widely used measure of the (equilibrium) dilational elasticity is the Gibbs elasticity defined by[30]

$$\varepsilon = \frac{\mathrm{d}\gamma}{\mathrm{d}\ln A} \cdots\cdots (2)$$

where A is the area per surfactant molecule at the interface. The Gibbs elasticity is derived from the equilibrium surface tension and thus involves the replacement of surfactant molecules at the interface by alkane molecules in the surface frozen phase. We find that the Gibbs elasticity calculated for the surface liquid and solid phases is about 50 mN m^{-1} at the critical micelle concentration (see Supporting Information) and is the same to within 3 mN m^{-1} in both phases. It would appear that neither the dilational elasticity measured by capillary wave methods (high frequency, small deformations) nor the Gibbs elasticity explains the difference in emulsion stability above and below the surface phase transition.

The drainage of the thin film between two mobile interfaces involves large deformations that might not be well-described by the linear response of capillary wave methods. Furthermore, if the deformation of the interface occurs on a timescale that is short compared to the relaxation

time of the monolayer (i.e. on timescales where the monolayer behaves as a solid), neither the surfactant nor the alkane within the surface frozen layer will exchange with the bulk. Under these circumstances the relevant elasticity is the 2-D compressional modulus of the surface frozen layer, which can be estimated from the slope of the pressure-area (π-A) isotherms of Langmuir monolayers in a structurally similar phase (LS). Typical values are $-d\pi/d\ln A = 1$ N m^{-1},[32,33] which is more than an order of magnitude larger than the Gibbs elasticity. The high mechanical elasticity of the surface frozen film would dominate the Gibbs elasticity and could lead to rigid interfaces and slow film drainage, as well as suppressing large area fluctuations that could lead to film rupture.

Two groups have reported faceting of alkane-in-water emulsions in the presence of surfactants at temperatures above the freezing point of the oil, which was ascribed to a surface frozen layer and ultralow interfacial tension[34,35] or to nucleation of a metastable rotator phase with a high bending rigidity.[36,37] Such facets could stabilise a planar water film between two oil droplets. The experiments presented in our paper are all at temperatures where the interfacial tension >> 1 mN m^{-1} and where capillary effects would be expected to dominate the bending modulus of the interface. Furthermore, ellipsometry results reported by Lei and Bain[15] and the data in Figure 1 show no evidence for interfacial crystallisation beyond a monolayer in the CTAB/tetradecane system. Consequently, we do not believe that faceting plays a role in emulsion stabilisation reported in this paper. Cholakova et al. have also argued that rotator phases nucleate from surfaces in drops of oil mixtures leading to droplet deformation at temperatures close to the melting point of the longer alkane.[38] Although we did not observe faceting in the C14-C16 mixtures by optical microscopy, we do not have definitive ellipsometry data on the liquid mixtures to exclude the possibility of faceting induced by plastic phases adjacent to the interface.

CONCLUSIONS

In this paper, we provide the first demonstration that the surface phase transition switched the kinetic stability of OW emulsion. To solve the problem that the existing solid film forming amphiphiles have very low water solubility and they do not form stable emulsion by their own, the surface freezing transition of cationic surfactant - alkane mixed adsorbed film was utilized. It was also demonstrated that the use of alkane mixture increases the temperature range of surface frozen film by the preferential incorporation of alkane molecules having chain length similar to the surfactant. The high mechanical elasticity of the surface frozen layer and resultant slow film drainage is proposed as the primary cause of the enhanced emulsion stability. To understand the effect of the mechanical property of the surface film in more detail, experiments are ongoing with the multilayer solid films composed of CTAC and hexadecanol at the $C12^{-}$water interface.

ASSOCIATED CONTENT

Supporting Information.

Supporting Information is available via the ACS Publication website at XXX.

AUTHOR INFORMATION

Corresponding Author

*E-mail; h.matsubarascc@chem.kyushu-univ.jp

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

HM appreciate for funding from MEXT/JSPS KAKENHI Grant Number JP 26400434 and 17H02943.

REFERENCES

(1) Matubayasi, N.; Motomura, K.; Aratono, M.; Matuura, R. Thermodynamic Study on the Adsorption of 1-Octadecanol at Hexane/Water Interface. *Bull. Chem. Soc. Jpn*. **1978**, *51*, 2800−2803.

(2) Ikenaga, T.; Matubayasi, N.; Aratono, M.; Motomura, K.; Matuura, R. Solvent Effect on the Adsorption of 1-Octadecanol at Oil/Water Interface. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 653−657.

(3) Berge, B.; Faucheux, L.; Schwab, K.; Libchaber, A. Faceted Crystal Growth in Two Dimensions. *Nature*. **1991**, *350*, 322−324.

(4) Overbeck, G. A.; Honig, D.; Mobius, D. Visualization of Firstand Second-Order Phase Transitions in Eicosanol Monolayers Using Brewster Angle Microscopy. *Langumir*. **1993**, *9*, 555−560.

(5) Henon, S.; Meunier, J. Phase Transitions in Gibbs Films: Star Textural Defects in Tilted Mesophases. *J. Chem. Phys.* **1993**, *98*, 9148−9154.

(6) Kato, T.; Matsumoto, N.; Kawano, M.; Suzuki, N.; Araki, T.; Iriyama, K. Transition to Three-Dimensional Structures in Monolayers of a Series of Long-Chain Acids on the Water

Surface by Compression Studied by Transmission Electron Microscopy and Atomic Force Microscopy. *Thin Solid Films*. **1994**, *242*, 223−228.

(7) Berge, B.; Konovalov, O.; Lajzerowicz, J.; Renault, A.; Rieu, J. P.; Vallade, M. Melting of Short 1-Alcohol Monolayers on Water: Thermodynamics and X-ray Scattering Studies. *Phys. Rev. Lett.* **1994**, *73*, 1652−1655.

(8) Lautz, C.; Fischer, Th. M.; Weygand, M.; Losche, M.; Howes, P. B.; Kjaer, K. Determination of Alkyl Chain Tilt Angles in Langmuir Monolayers: A Comparison of Brewster Angle Auto Correlation Spectroscopy and X-ray Diffraction. *J. Chem. Phys.* **1998**, *108*, 4640−4646.

(9) Vollhardt, D.; Fainerman, V. B.; Emrich, G. Dynamic and Equilibrium Surface Pressure of Adsorbed Dodecanol Monolayers at the Air/Water Interface. *J. Phys. Chem. B* **2000**, *104*, 8536−8543.

(10) McKenna, C.; Knock, M. M.; Bain, C. D. First-order Phase Transition in Mixed Monolayers of CTAB and Tetradecane at the Air–Water Interface. *Langmuir* **2000**, *16*, 5853-5855.

(11) Sloutskin, E; Sapir, Z; Bain, C.D.; Lei, Q.; Wilkinson, K.M., Taman, L.; Deutsch, M.; Ocko, B.M. Wetting, mixing, and phase transitions in Langmuir-Gibbs films. *Phys. Rev. Lett*. **2007**, *99*, 136102.

(12) Sloutskin, E.; Sapir, Z.; Tamam, L.; Ocko, B. M.; Bain, C. D.; Deutsch, M. Freezing Transition of Langmuir−Gibbs Alkane Films on Water. *Thin Solid Films* **2007**, *515*, 5664−5668.

(13) Ocko, B.M.; Wu, X.Z.; Sirota, E.B.; Sinha, S.K.; Gang, O.; Deutsch, M. Surface freezing in chain molecules: normal alkanes. *Phys. Rev. E*, **1997**, *55*, 3164–3182.

(14) Gang, O.; Wu, X.Z.; Ocko, B.M.; Shirota, E.B.; Deutsch, M. Surface freezing in chain molecules. II. Neat and hydrated alcohols, *Phys. Rev. E*, **1998**, *58*, 6086-6100.

(15) Lei, Q.; Bain, C. D. Surfactant-Induced Surface Freezing at the Alkane−Water Interface. *Phys. Rev. Lett.* **2004**, *92*, 176103−1−4.

(16) Sloutskin, E.; Bain, C. D.; Ocko, B. M.; Deutsch, M. Surface Freezing of Chain Molecules at the Liquid−Liquid and Liquid−Air Interfaces. *Faraday Discuss.* **2005**, *129*, 339 −352.

(17) Tamam, L.; Pontoni, D.; Sapir, Z.; Yefet, S.; Sloutskin, E.; Ocko, B. M.; Reichert, H.; Deutsch, M. Modification of Deeply Buried Hydrophobic Interfaces by Ionic Surfactants. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 5522−5525.

(18) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; Wiley Interscience: Hoboken, NJ, 2004.

(19) Gamboa, C.; Rios, H.; Sanchez, V. Surfactant Aggregation in Formamide. *Langmuir* **1994**, *10*, 2025−2027.

(20) Tokiwa, Y.; Sakamoto, H.; Takiue, T.; Aratono, M.; Matsubara, H. Effect of Alkane Chain Length and Counterion on the Freezing Transition of Cationic Surfactant Adsorbed Film at Alkane Mixture−Water Interfaces. *J. Phys. Chem. B* **2015**, *119*, 6235-41.

(21) Binks, B. P. *Modern Aspects of Emulsion Science*; The Royal Society of Chemistry: Cambridge, U. K., **1998**.

(22) Evans, F. D.; Wennerström, H. *The Colloidal Domain 2nd edition*; Wiley-VCH: New

York, USA, **1999**.

(23) Lide, D. A. *Handbook of Chemistry and Physics 87th edition*; CRC Press: Boca Raton, U.S.A., 2006.

(24) Verwey, E.J.W.; Overbeek, J.Th.G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, Netherlands, 1948.

(25) Ohtomi, E.; Ikeda, N.; Tokiwa, Y.; Watanabe, I.; Tanida, H.; Takiue, T.; Aratono, M.; Matsubara, H. Thin-Thick Transition of Foam Film Driven by Phase Transition of Surfactant-Alkane Mixed Adsorbed Film. *Chem. Lett.* **2012**, *41*, 1300-3.

(26) Bergeron, V. Disjoining Pressures and Film Stability of Alkyltrimethylammonium Bromide Foam Films. *Langmuir*, **1997**, *13*, 3474-3482.

(27) Weaire, D.; Hutzler, S. *The Physics of Foams;* CLARENDON: Oxford, U.K., 1999.

(28) Denkov, N.D.; Tcholakova, S.; Golemanov, K.; Ananthpadmanabhanb, K.P.; Lipsc, A. The role of surfactant type and bubble surface mobility in foam rheology. *Soft Matter* **2009**, *5*, 3389-3408.

(29) Muñoz, M. G.; Luna, L.; Monroy, F.; Rubio, R. G.; Ortega, F. Viscoelastic behavior of 1-dodecanol monolayers undergoing a liquid–solid phase transition: a surface quasielastic light scattering study. *Langmuir*, **2000**, *16*, 6657–6666.

(30) Gibbs, J. W. *The Scientific Papers of J. Willard Gibbs*; Dover: New York, U.S.A.; 1961.

(31) Casson, B. D.; Braun, R.; Bain, C. D. Phase transitions in monolayers of medium-chain alcohols on water studied by sum-frequency spectroscopy and ellipsometry. *Faraday Discuss.* **1996**, *104*, 209-229.

(32) Gaines Jr, G.L. *Insoluble Monolayers at Liquid–Gas Interfaces*; Interscience: New York, 1966.

(33) Lawrie, G. A.; Barnes, G. T. “Octadecanol monolayers: the phase diagram” J. Colloid Interface Science 1994, 162, 36–44.

(34) Guttman, S.; Sapir, Z.; Schultz, M.; Butenko, A.V.; Ocko, B.M.; Deutsch, M.; Sloutskin, E. How faceted liquid droplets grow tails, *PNAS*, **2016**, *113*, 493-496.

(35) Guttman, S.; Sapir, Z.; Ocko, B.M.; Deutsch, M.; Sloutskin, E. Temperature-tuned faceting and shape changes in liquid alkane droplets. *Langmuir*, **2017**, *33*, 1308-1314.

(36) Denkov, N.; Cholakova, D.; Tchokakova, S.; Smoukov, S.K. On the Mechanism of Drop Self-Shaping in Cooled Emulsions, *Langmuir*, **2016**, *32*, 7985-7991.

(37) Denkov, N.; Tcholakova, S.; Lesov, I.; Cholakova, D.; Smoukov, S. K. Self-shaping of oil droplets via the formation of intermediate rotator phases upon cooling. *Nature* **2015**, *528*, 392−395.

(38) Cholakova, D.; Valkova, Z.; Tcholakova, S.; Denkov, N.; Smoukov, S.K. “Self-Shaping” of Multicomponent Drops, *Langmuir*, **2017**, *33*, 5696-5706.

TOC Image